[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND THE WESTERN ELECTRIC COMPANY, INCORPORATED]

THE VAPOR PRESSURES OF ROCHELLE SALT, THE HYDRATES OF SODIUM AND POTASSIUM TARTRATES AND THEIR SATURATED SOLUTIONS

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In an investigation of the vapor pressure of Rochelle salt, $NaKC_4H_4O_6.4H_2O$, it was found that reproducible values could not be obtained if the crystals had been heated previously at any time above 40°. This is in accord with the observation of van Leeuwen[1] that Rochelle salt can exist alone in a saturated solution only below 40°. At this temperature sodium tartrate is deposited, being less soluble than the potassium salt, and the solution becomes saturated with respect to both Rochelle salt and sodium tartrate. He found also that the saturated solution of Rochelle salt could not exist as such above 55°. At this temperature it decomposed completely to the sodium and potassium tartrates. This same transition was observed in the crystals when they were held at 55–58°. The crystals became cloudy and, according to van Leeuwen, one could see, microscopically, the needle-like crystals of sodium tartrate which separated. In view of these observations, it seemed advisable to determine also the vapor pressures of the sodium salt, $Na_2C_4H_4O_6.2H_2O$, the potassium salt, $K_2C_4H_4O_6.{}^1/_2H_2O$, and their saturated solutions.

The static method with mercury as the enclosing liquid was chosen for these measurements. The volume of the bulb of the tensimeter was about 30 cc. of which one-half to two-thirds was filled with vapor. The tensimeter was completely immersed in an electrically controlled thermostat which could be held at the temperatures of measurement ± 0.1°. The thermometers were all mercury in glass and were calibrated at the ice point and at the transition point of sodium sulfate decahydrate, 32.38°. The hydrates were recrystallized from the commercial salts of highest purity obtainable. Duplicate determinations were made using different amounts of salt. The enclosed "permanent gas" was removed by washing out the apparatus at low pressures with water vapor. Reading of the pressures was accomplished with the aid of a micrometer depth gage[2] to ± 0.1 mm.

The experimental results are given in Table I and shown in Fig. 1; t_w is the temperature at which water has the same vapor pressure[3] as either the hydrate or the saturated solution at their respective temperatures t. The data are plotted according to the method employed by

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[1] van Leeuwen, *Z. physik. Chem.*, **23**, 33 (1897).

[2] Ferguson, *J. Washington Acad. Sci.*, **10**, 285 (1920).

[3] Scheel and Heuse, *Ann. Physik*, [4] 31, 715 (1910).

Johnston,[4] who pointed out that when t is plotted against t_w the resulting graph for such vapor-pressure data is a straight line which may be represented by an equation $t = at_w + b$, where a represents the slope of the line and b the value of t when t_w is zero. These constants are given in Table I, and also the values of t calculated in each case from the appropriate equation. In the fifth column the differences between the observed and calculated values are given. The differences are quite irregular and, with the exception of the data on the hydrate of potassium tartrate, are probably

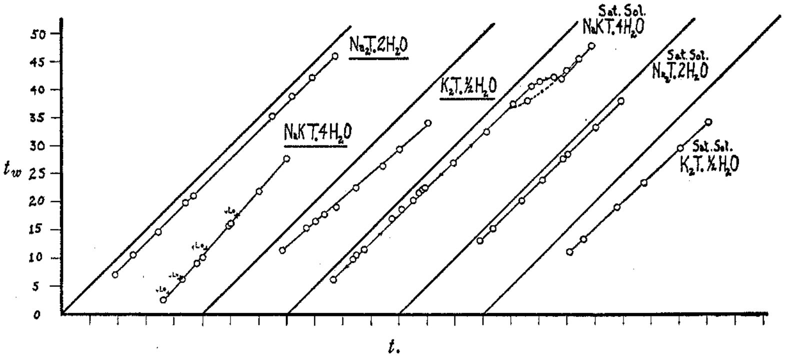

Fig. 1.—Graphical representation of vapor-pressure data of Rochelle salt, the hydrates of sodium tartrate and potassium tartrate, and of their saturated solutions; t_w is the temperature at which water has the same vapor pressure as either the hydrate or the saturated solution at their respective t. For simplification all six curves have been included on one diagram. In order that the curves should not overlap, it is necessary to have five zero points which are indicated where the heavy black lines cut the t axis. For these heavy lines $t = t_w$. Intervals have been indicated every 5° on the t axis.

TABLE I

OBSERVED VAPOR PRESSURES OF ROCHELLE SALT, THE HYDRATES OF SODIUM TARTRATE, AND POTASSIUM TARTRATE AND THEIR SATURATED SOLUTIONS

Temperature °C. $t_{obs.}$	Pressure mm. Hg p	Temperature at which vapor pres. of water = p t_w	$t_{calc.} = at_w + b$	$t_{obs.} - t_{calc.}$
	ROCHELLE SALT		$t_{calc.} = 0.88t_w + 16.0$	
18.0	5.5	2.5	18.2	−0.2
21.4	7.1	6.2	21.4	± .0
24.0	8.6	9.0	23.9	− .1
25.1	9.3	10.1	24.8	+ .3
29.7	13.4	15.7	29.7	± .0
30.1	13.7	16.1	30.0	+ .1
35.1	19.6	21.8	35.0	+ .1
40.0	27.9	27.7	40.2	− .2

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[4] Johnston, *Z. physik. Chem.*, **62**, 330 (1908). This is essentially "Dühring's Rule," Dühring, *ibid.*, **13**, 492 (1894); **65**, 338 (1909).

TABLE I (*Continued*)

Temperature °C. $t_{obs.}$	Pressure mm. Hg p	Temperature at which vapor pres. of water = p t_w	$t_{calc.} = at_w + b$	$t_{obs.} - t_{calc.}$
SODIUM TARTRATE			$t_{calc.} = 1.00t_w + 2.3$	
9.1	7.5	7.0	9.3	−0.2
12.7	9.6	10.6	12.9	− .2
17.2	12.5	14.6	16.9	+ .3
22.0	17.3	19.8	22.1	− .1
23.5	18.6	21.0	23.3	+ .2
37.5	42.8	35.3	37.6	− .1
41.0	52.3	38.9	41.2	− .2
44.6	62.3	42.2	44.5	+ .1
48.6	75.6	46.0	48.3	+ .3
POTASSIUM TARTRATE			$t_{calc.} = 1.15t_w + 1.2$	
14.2	10.1	11.4	14.3	− .1
18.5	13.0	15.3	18.8	− .3
20.1	14.0	16.4	20.1	± .0
21.7	14.8	17.3	21.1	+ .6
23.9	16.4	18.9	23.0	+ .9
27.3	20.3	22.4	27.0	+ .3
32.0	25.6	26.3	31.5	+ .5
35.4	30.6	29.3	35.0	+ .4
40.0	39.9	34.0	40.3	− .3
SATURATED SOLUTION OF ROCHELLE SALT[a]			$t_{calc.} = 1.03t_w + 1.7$	
8.3	7.1	6.2	8.1	+ .2
11.8	9.1	9.8	11.8	± .0
12.4	9.5	10.5	12.5	− .1
13.8	10.2	11.5	13.6	+ .2
18.7	14.4	16.9	19.1	− .4
20.4	16.1	18.6	20.9	− .5
23.5	19.2	21.5	23.9	− .4
24.1	19.8	22.0	24.4	− .3
24.6	20.3	22.4	24.8	− .2
29.7	26.6	26.9	29.4	+ .3
35.6	36.7	32.5	35.2	+ .4
40.3	48.2	37.4	40.3	± .0
43.6	57.2	40.6	..	...
45.1	59.5	41.4	..	...
47.6	62.1	42.2	..	...
49.0	61.3	41.9	..	...
52.1	73.9	45.5	..	...
54.3	82.8	47.8	..	...
49.9	66.3	43.4	..	...
46.1	56.4	40.4	..	...
42.9	49.8	38.0	..	...
22.5	17.7	20.2	22.5	± .0
SATURATED SOLUTION OF SODIUM TARTRATE			$t_{calc.} = 1.02t_w + 1.1$	
14.4	11.4	13.2	14.5	− .1
16.8	13.1	15.4	16.8	± .0

TABLE I (*Concluded*)

Temperature °C. $t_{obs.}$	Pressure mm. Hg p	Temperature at which vapor pres. of water = p t_w	$t_{calc.} = at_w + b$	$t_{obs.} - t_{calc.}$
22.0	17.9	20.3	21.8	+ .2
25.6	22.2	23.9	25.4	+ .2
29.3	27.8	27.7	29.3	± .0
30.2	29.2	28.5	30.1	+ .1
35.2	38.5	33.4	35.1	+ .1
39.6	49.9	38.1	39.9	− .3
SATURATED SOLN. OF POTASSIUM TARTRATE			$t_{calc.} = 1.07t_w + 3.6$	
15.5	9.9	11.1	15.5	± .0
17.9	11.5	13.3	17.9	± .0
23.9	16.5	19.0	24.0	− .1
28.8	21.6	23.4	28.7	+ .1
35.2	30.9	29.5	35.2	± .0
40.2	40.3	34.2	40.3	− .1

[a] At temperatures above 40° the solution is no longer a saturated solution of Rochelle salt, but is a solution saturated with two salts, sodium tartrate and Rochelle salt, and containing some potassium tartrate.

not greater than errors in reading temperature and pressure. Values of the vapor pressure of these hydrates and of their saturated solutions at 5° intervals from 15° to 40° were calculated from the equations (Table I) and are given in Table II.

TABLE II

INTERPOLATED VALUES OF VAPOR PRESSURES OF ROCHELLE SALT, THE HYDRATES OF SODIUM TARTRATE AND POTASSIUM TARTRATE, AND THEIR SATURATED SOLUTIONS FROM 15–40°

Temperature °C.	Vapor pressure of					
	Hydrates			Solutions		
	Roch. salt	Sod. tar.	Pot. tar.	Roch. salt	Sod. tar.	Pot. tar.
15	4.1	11.0	10.5	11.2	11.7	9.6
20	6.3	15.2	13.9	15.3	16.0	13.0
25	9.3	20.7	18.3	20.7	21.6	17.5
30	13.5	27.9	23.8	27.7	29.0	23.2
35	19.2	37.1	30.7	36.5	38.2	30.6
40	27.1	48.9	39.2	47.6	50.2	39.9

On Fig. 1 are also shown four points representing vapor pressures of Rochelle salt as determined by van Leeuwen[1] by a static method using oil as the enclosing liquid. They fall on the curve best fitting the results of our measurements. These vapor pressures of Rochelle salt which are given in Table I were determined on the hydrate which had at no time been heated above 40°. When the salt had been heated above this temperature the vapor pressure at 20° reached an apparently constant value which ranged from 12.6 mm. to 6.6 mm., depending probably on both the time which it had been held at this temperature and the maximum temperature to which it had been raised. The correct value for Rochelle salt at 20° is 6.3 mm. It is also evident from Fig. 1 that the vapor-pressure measurements on the saturated solution of Rochelle salt show that the solid phase in such a solution is unstable above 40° as previously pointed out by van Leeuwen. The fact that the points obtained with decreasing temperature in the transition range fall on a different curve from that obtained with increasing temperature in the same range indicates that equilibrium had not been reached.

Summary

Vapor pressures of Rochelle salt, the hydrates of sodium tartrate and potassium tartrate, and their saturated solutions have been determined by a static method at several temperatures between 15° and 40°.

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THE RADICAL THEORY IN MODERN CHEMISTRY[1]

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In a compound containing a large number of atoms a corresponding number of valence bonds exist among the constituent atoms. In the reaction of such compounds not all the valence bonds, in general, break down; but more often a few, or even a single bond, may break down with the formation of new compounds in which some of the original combinations remain. The different valence bonds in a compound thus have varying degrees of stability, and those atoms which are joined by the more stable bonds remain combined with one another throughout a series of reactions. These relatively stable groups are what are commonly termed radicals. It is the purpose of the present paper to determine in how far the properties of compounds may be interpreted in terms of those of the more stable groups from which these compounds are built up.

I have shown elsewhere that the properties of compounds of the binary type may be interpreted in terms of the electro-affinities of the constituent elements.[2] With respect to their electro-affinities, the elements may be arranged in a series from the most electropositive to the most electronegative. This series is a twofold one since, with the exception of the very electropositive and the very electronegative elements, all elements may carry negative as well as positive charges, and thus appear in both series. These elements appearing in both series, which have been termed amphoteric elements, comprise the major portion of the elements, and the

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[1] This paper comprises the subject matter of the Nichols Medal Address delivered before the New York Section of the American Chemical Society, on March 7, 1924.

[2] Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 379 (1924).